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The use of microvoids to toughen polymers

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The concept of microvoid toughening of polymers has been proposed by several investigators. This investigation illustrates the similarities between the function of rubber particles in rubber-toughened plastics with that of microvoids. While previous researchers created microvoids within polymeric materials by means of non-adhering particles, our novel approach is based on using hollow plastic micro-spheres to generate holes. An epoxy polymer is used as a model polymer matrix. The results of this investigation show that hollow plastic particles toughen the epoxy resin in the same manner as rubber particles. Surprisingly, mechanical characterization of modified blends revealed that the use of hollow plastic micro-spheres provides greater yield strength than that of similar blends with equivalent rubber content.

(Keywords: rubber-toughened polymers, hole toughening; epoxy; hollow latex particles)

Introduction

Rubber modification, i.e. addition of a rubbery particulate phase, has been found a very successful approach to overcome the inherent brittleness of many engineering polymers. The origin of this improvement in crack growth resistance is believed to be cavitation of rubber particles followed by shear deformation[1–3] or crazing[4,5] of the matrix, depending upon the nature of the polymer. This scenario might be accomplished by employing holes instead of rubber particles. Indeed, some researchers have studied the concept of microvoid toughening in polymers, either theoretically[6,7] or experimentally[8,9].

Theoretical efforts regarding the microvoid toughening concept have focused on the use of finite elemental analysis techniques[6,7]. Guild and Young[6] claimed that rubber particles behave like holes, since their finite element analysis revealed no considerable difference between the two in terms of concentrating stress on the surrounding matrix. Fukui *et al.*[7] also conducted a finite element technique to compare the function of rubber particles with that of holes in a nylon matrix. The study showed that rubber particles provide a more favourable situation for toughening than voids, since the latter can cause cracking of the matrix at lower strain levels.

Experimental efforts in this regard have focused on using non-adhering particles to generate voids in the polymer matrix[8,9]. This approach, however, has been shown not to be adequate in some cases. Sue *et al.*[8], for example, modified PC by addition of PE particles. In contrast to the general speculation of poor adhesion between PC and PE due to their incompatibility, these researchers found a relatively strong bonding between the two phases. Although Sue *et al.*[8] observed that PE particles debond from the matrix at higher stresses, they were uncertain whether real holes can be as effective as PE in the toughening of PC. Huang and Kinloch[9] created holes in an epoxy using unreactive liquid rubber. This approach improved the fracture toughness of their neat epoxy resin significantly and illustrated the potential for voids to toughen brittle polymers. Despite having no rubber modified epoxy to compare with, Huang and Kinloch[9] speculated a higher fracture toughness for a rubber modified epoxy due to the bridging efficiency of rubber particles. More recently, Huang *et al.*[10] studied the influence of adhesion at the rubber particle/matrix interface using liquid rubbers with different degrees of reactivity. No conclusive comparison between strongly and poorly adhered rubber particles was made in that study since the volume fraction and size of the precipitated phases varied in different cases; a common problem when using liquid reactive elastomers.

A novel approach to examine the concept of microvoid toughening of polymers is employed in this study. The basis of this investigation is the use of hollow latex particles to toughen an epoxy resin. The particular hollow latex particles used in this study are commercially available and have a narrow size distribution. Understanding the mechanism of toughening in epoxies modified with hollow plastic particles provides further insight about the role of cavitation in rubber-toughened polymers. Additionally, this study may introduce a new family of engineering polymers with improved toughness and reduced density applicable for advanced composite materials.

Experimental

The epoxy system selected for this study is based on a diglycidyl ether of bisphenol A (DGEBA) epoxy with an epoxy equivalent weight of 187 g mol^{-1} (DER 331 resin from Dow Chemicals). The curing agent used is aminoethyl piperazine (AEP) from Air Products and Chemicals. A stoichiometric ratio of curing agent is mixed with resin at room temperature and poured into an aluminium mould. The cast material is allowed to gel

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Table 1 Description of the toughening agents used

Modifier	Description of modifier
CTBN	Carboxyl-terminated liquid copolymer of butadiene and acrylonitrile from BF Goodrich (Hycar CTBN 1300X8)
MBS	Structured core/shell latex particles comprised of a methacrylated butadiene–styrene copolymer with acid functionality from Rohm & Haas (Paraloid EXL-2611)
HLP-0.4	Hollow latex particles with a styrene–acrylic shell from Rohm & Haas (Ropaque OP-62)
HLP-1.0	Similar to HLP-0.4 but larger in size (Ropaque HP-91)

for 1 h at room temperature and then post-cured for 2 h at 100°C. The same curing schedule is employed for the toughened epoxies as well. Toughening agents used include two conventional rubber modifiers and two types of hollow latex particles. *Table 1* describes the characteristics of the toughening agents used.

The concentrations of modifiers are 10 phr for CTBN and 10 vol% for preformed hollow and MBS particles. CTBN oligomer was pre-reacted with the resin prior to adding curing agent. MBS latex particles were first suspended in acetone and then the acetone was substituted by epoxy under vacuum. Particles were finally pre-reacted with epoxy. This approach was found to be the best method for uniformly dispersing solid latex particles with acid functionality in epoxy matrices. A freeze drying technique was employed to dry emulsions containing hollow particles. Dried powders were then mixed with epoxy at room temperature for more than 24 h to obtain a uniform suspension.

The cured materials were characterized using a variety of techniques. Glass transition temperatures were determined by differential scanning calorimetry (d.s.c.) at a heating rate of 10°C min^{-1}. Yield strength measurements were performed in compression in accordance to the ASTM D695 test procedure. The ASTM D5045 guideline was followed to measure the plane strain fracture toughness in this study. Fracture toughness values were determined using pre-cracked, single edge notched (SEN) specimens in three-point bending (3PB) geometry. Fracture surfaces were examined using a scanning electron microscope (SEM). The double-notched four-point bend method, in conjunction with transmission optical microscopy (TOM), was employed to study the crack tip damage zone of modified materials. This is the same technique used by Pearson and Yee[2] for elucidation of toughening mechanisms.

Results

The d.s.c. analyses revealed glass transition temperatures of 105 ± 1°C for all modified and unmodified materials, indicating no change in the chemical structure of the epoxy matrix via rubber/void modification.

Results of mechanical testing, along with the particle sizes of the modifiers used, are shown in *Table 2*. The shell thickness of the hollow particles is about one-tenth of their outer diameter. The results of yield strength measurements, as shown in *Table 2*, indicate a decline in the yield strength of the neat resin by employing either type of modifiers. The results of the fracture toughness evaluations, however, show a significant increase in the crack growth resistance of the neat epoxy by incorporation of either rubber particles or voids (*Table 2*).

Table 2 Mechanical characterization of neat and modified epoxy blends

Modifier	Particle size[a] (μm)	Fracture toughness (MPa $m^{0.5}$)	Yield strength (MPa)
None	None	0.85	90.0
CTBN	0.55	2.05	71.0
MBS	0.2	2.20	82.0
HLP-0.4	0.4	2.30	84.5
HLP-1.0	1.0	1.95	83.0

[a] Particle size of CTBN modified material was measured using SEM micrographs taken from the fast fracture region

The toughening mechanisms were elucidated using SEM and TOM. SEM micrographs of the fracture surfaces, taken from the stress whitened zone of the modified epoxies, showed uniformly distributed second phase particles and perfect adhesion between the particles and the matrix. Hollow particles were also found intact and the epoxy had not penetrated into the cavities prior to gelation. This fact is seen in *Figure 1* which illustrates the fracture surface of epoxy modified with 1 μm hollow particles (HLP-1.0). TOM of thin sections of double-notched four-point bend specimens revealed massive shear banding at the crack tips of modified materials. *Figure 2* represents the TOM micrograph taken from the mid-plane at the crack tip of epoxy modified with HLP-1.0 particles which is viewed using cross-polarized light. Birefringence of the damage zone in this figure indicates that the matrix has shear yielded. The same pattern has been reported by other investigators as the sign of shear banding[2,8].

Discussion

Observation of shear bands at the crack tip damage zone of both rubber and microvoid modified materials indicates a similar toughening mechanism operating in both systems. Similarly, fracture toughness values shown in *Table 2* indicate no essential difference between rubber and hollow particles in improving the fracture toughness of this epoxy system. In other words, microvoids toughen the present matrix in the same way and to almost the same magnitude as rubber modifiers. Modest differences

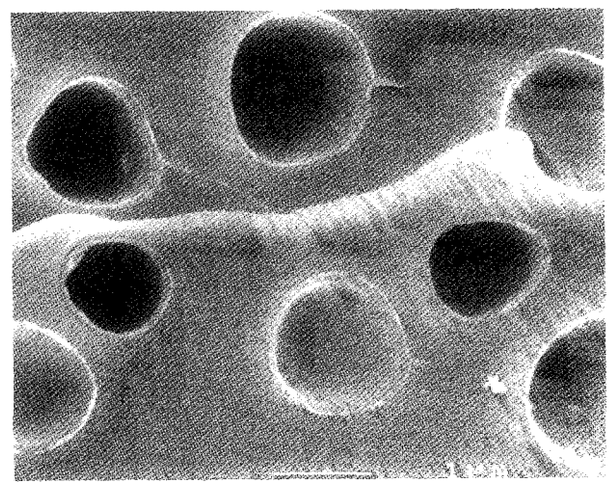

Figure 1 SEM micrograph of the fracture surface of epoxy modified with 10 vol% HLP-1.0 particles taken from the stress whitened zone

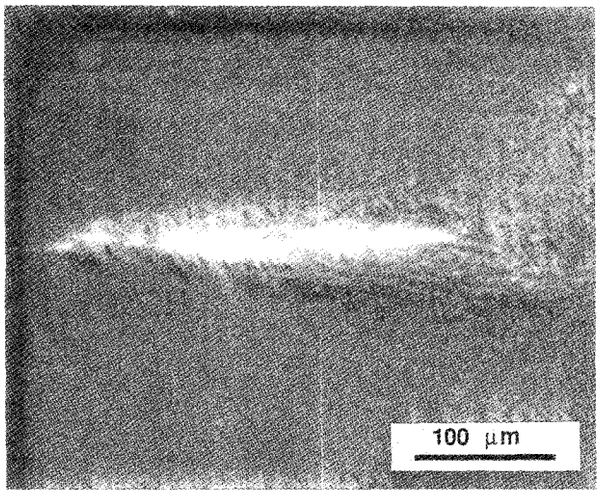

Figure 2 TOM micrograph of the crack tip damage zone of epoxy modified with 10 vol% HLP-1.0 particles. Micrograph is taken in the mid-plane of the double-notched four-point bend specimen and viewed under cross-polars

among the fracture toughness data can be attributed to the particle size effect. Although modifiers used are nearly the same size, the smaller particles seem to induce a higher fracture toughness. Therefore, the results of this study refute the idea of Huang and Kinloch[9] in that particle bridging is considered as an additional toughening mechanism in rubber-modified epoxies, compared to that of hole-toughened resins.

Another point to be discussed is the possible influence of the shell of hollow plastic particles in fracture toughness of the modified blends. One important point here is the fact that these particles have a glassy polymer shell with similar elastic properties to that of the epoxy matrix. Therefore, the presence of this shell cannot make a considerable difference in the stress distribution around the holes. Secondly, since the shell material is thin, i.e. one-tenth of the particle size, it can easily deform and follow the plastic dilation of the surrounding matrix. Indeed, our SEM study suggests good adhesion between the hollow particles and the epoxy matrix within the stress whitened zone (*Figure 1*). In addition. MBS particles used in this study also have a glassy PMMA shell which could play a similar role to that of the hollow particles, if there is any.

It should be mentioned that the materials modified with preformed particles have very close compression yield strengths (*Table 2*). Based on this observation, one may claim that rubber particles and microvoids have the same influence on the yield behaviour of the present epoxy under uniaxial test conditions, i.e. parallel to the proposal of Guild and Young[6]. CTBN rubber, however, lowered the yield strength of the epoxy matrix significantly, different to that of other modifiers. This difference cannot be attributed to a matrix plasticization effect, since d.s.c. measurements revealed the same glass transition temperature for all modified materials. A possible rationale for this observation could be the influence of CTBN rubber on the sub-T_g relaxation of the epoxy matrix. This possible effect has not been evaluated.

The results of this investigation identify a new approach for toughening of engineering polymers. Such an approach has several advantages, including: (1) comparable or even higher mechanical properties than that of the conventional rubber modifiers; (2) reduced density of the blend; and (3) no sensitivity to u.v. light radiation, i.e. better weathering resistance. Epoxies toughened with hollow latex particles should also display better low-temperature performances than that of rubber-toughened epoxies at service temperatures below the T_g of the rubber particles.

Future research should consider improvements in the processability of hollow latex particles. Having a cross-linked shell and either reactive or polar groups on the outer surface of the particles will ease processing and dispersion in the polymer matrix. A following publication[11] will examine the effect of volume fraction of the modifiers used on the fracture behaviour of the present epoxy matrix.

Conclusions

Two types of hollow latex particles are employed as toughening agents in an epoxy matrix for the first time. The influence of these modifiers on mechanical properties of the matrix are compared with that of two rubber tougheners. The conclusions of this study are:

(1) Hollow plastic micro-spheres toughen brittle epoxies in the same manner as rubber particles.
(2) No superiority of rubber particles over voids in toughness improvement was found.
(3) Epoxies modified with hollow latex particles have a higher yield strength than conventional CTBN-modified epoxies.

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